SOLID - LIQUID SEPARATION OF DAIRY MANURE: DISTRIBUTION OF COMPONENTS AND METHANE PRODUCTION.

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Abstract

Chemical treatment and screening can be an effective technique for separation of dairy cattle manure into a liquid fraction (LF) and a nutrient-rich solid fraction (SF). The optimum loading of a strong cationic polyacrylamide was found to be 43.9 g kg^{-1} of dry excreta. The separated SF contained 29.1% of the initial mass present in the manure and the chemicals added. The Volatile Solids (VS) / Total Solids (TS) ratio, which was 0.78 for the manure, rose to 0.82 for the SF and decreased to 0.63 in the LF. Furthermore, the SF retained 76.1, 79.9, 59.4 and 87.4% of TS, VS, Total Kjeldahl Nitrogen and Total Phosphorus, respectively. In the LF, the ratio of filtrate chemical oxygen demand ($COD_{filtrate}$) and COD due to volatile fatty acids (COD_{VFA}) in relation to total COD (COD_T) were 0.86 and 0.76, respectively. The percentage of anaerobically biodegradable chemical oxygen demand (COD_{BD}) for the LF was 83.0%. Treatment of the LF in high loading anaerobic reactors would be possible due to these COD characteristics. Specific methane production in terms of VS for the separated LF was 0.580 m^3 kg^{-1}. For dairy manure and SF, it was 0.320 and 0.258 m^3 kg^{-1}, respectively.

Keywords: dairy manure; solids removal; polyacrylamide; liquid fraction; anaerobic biodegradability.

1. Introduction

Intensive dairy cattle farms generate vast amounts of animal slurry with a low concentration of nutrients. Land application, the traditional dairy manure management strategy, is posing serious environmental pollution problems [1, 2]. In wet climate zones, for example, the liquid fraction of manure is responsible for superficial and subterranean water pollution. These environmental problems are difficult to solve due to the high contents of organic matter and nutrients [3].

An analysis of pre-disposal conditioning treatments of cattle manure has shown that the separation of liquid and solid fractions of manure is one of the most suitable upstream operations. The size of manure storage vessels is reduced, which implies significant cost savings [4]. The separated solid fraction (SF) has relatively small volume and is suitable either for the production of compost or anaerobic dry digestion [5]. The shipping cost for stabilised solid fraction from intensive dairy farms zones to others with lack in nutrients will be diminished [6] and the liquid fraction (LF) offers the benefit of more economical and easier treatment options [7].

The analysis of particle size distribution in fresh dairy manure have shown that Total Solids (TS) and Volatile Solids (VS) are almost equally contained in particles larger than 1 mm and smaller than 0.053 mm. Usually less than 25% of the TS and VS are contained in particles smaller than 1 mm and larger than 0.053 mm [8]. It was found that 60% of TS, 86% of Total Kjeldahl Nitrogen (TKN) and 94% of Total Phosphorus (TP) were contained in particles with a size smaller than 0.5 mm [9]. Other authors consider necessary to remove all particles smaller than 0.25 mm as well as coarse particles in order to effectively control odour and reduce nitrogen and phosphorus contents of LF in manure [10].

Screens are the most extensively used separators. The performance of screen separators is basically determined by mesh size, velocity flow, solids concentration and particle size distribution in manure [11]. Smaller screen sizes achieve higher solid removal percentages, but the SF presents a higher moisture content. As manure flow increases, this effect becomes more pronounced [12]. When manure is collected by flushing, it is more dilute and it filters better through the sieve. The SF separated contained lower suspended solids and nutrients than the SF from the higher total solids manure, due to the fact that the additional water washed more fine solids and nutrients through the screen [13]. A review of the performance of manure separator devices has been described in the literature by Hjorth et al. [14]. According to these authors, centrifugation is the most effective technique for removing dry matter (DM) and Total Phosphorous (TP), whereas filtration results in lower efficiency for the removal of DM and nutrients.

Coagulation is a process of aggregating suspended (colloidal or dispersed) particles to form settable flocs through addition of electrolytes or organic polymers. Most suspended particles in wastewaters with a pH greater than four have a negative charge, thus the electrolytes used are inorganic salts of multivalent cations such as iron, aluminium and calcium. The flocculation process, agglomeration of coagulated particles into larger, rapidly settling flocs, is effected through particle-particle interaction through attachment to long-chain polymer molecules. Cationic polyacrylamides (PAM) with moderate charge density are more effective than polymers with higher charge density for solids and nutrients removal [11, 15].

The conventional treatment applied to animal manures has been the anaerobic digestion process, which permits the recovery of biodegradable organic matter in the form of methane in the biogas, whereas the nutrients remain in the stabilised manure, except volatilised ammonia [16, 17]. If the LF obtained by screening is subjected to an anaerobic digestion process in low load reactors, pump and piping operational problems are lower, as well as fouling into the reactor, but organic matter removal in terms of VS did not reach values higher than 45% [7, 18]. If manure is very diluted, the LF can be treated in high loading anaerobic reactors, but a previous study [19] only reached 41.5% of COD removal efficiency. If higher organic matter removal efficiencies are desired in the anaerobic digestion process, a LF with lower suspended solids content would be necessary; in this case, screening should not be the only pre-treatment performed.

In Cantabria, a region in northern Spain, about 350,000 dairy cows generate around 4,500,000 t per year of semi-liquid manure (7-14% TS). Most of the intensive farming is operated on the coastal flatlands, which are tourism areas. Manure storage capacity is limited and there is not enough land available for waste disposal by direct application during those periods when the soil benefits from nutrient additions, which leads to environmental damage. In humid areas, especially those with steep terrain (as is the case in many parts of Cantabria), the liquid fraction of manure is responsible for part of the pollution found in superficial and underground waters.

The development of solutions for this problem was the motivation for the present work. The overall process undergone by the manure was considered: once the initial hydrolytic and acidogenic stages have taken place in a controlled manure pit [20], solid and liquid fractions of manure can be separated and then stabilised by means of biological treatments. In order to obtain a liquid fraction with the majority of its COD in soluble and highly biodegradable form to be treated in high-load anaerobic reactors, chemical reactives have to be used. Anaerobic digestion in dry fermentation batch systems is an attractive

alternative for the solid fraction [21]. Once this material has been digested it can be used both as a fertilizer or soil conditioner. However, anaerobic treated effluents of the LF can not be discharged to public water bodies without further treatment, according to present environmental regulations. Therefore, additional decontaminating processes have to be applied to the effluent, alone or mixed with other wastewaters.

The objectives of the present work are:

(1) To determine the optimum dose of polyacrylamide needed for achieving the separation of SF and LF of dairy cattle manure.

(2) To determine the distribution of mass, TS, VS, TKN and total phosphorus from dairy cattle manure in SF and LF.

(3) To determine the distribution of the methanogenic productivities of dairy cattle manure and its solid and liquid fractions.

(4) To characterise the COD_{total}, $COD_{filtrate}$, COD_{VFA} and $COD_{biodegradable}$ of the LF with a view to the possibility of treating it in high load anaerobic digesters.

2. Material and methods

2.1. Manure collection

For this work, manure with a TS concentration of 10-14% was collected from a dairy farm in the Santander area (Northern coast of Spain). There were 140 lactating cows, 40 dry cows, 80 heifers and 30 calves. Lactating cows had a mean age of four years, weighing between 600-700 kg. Cows diet consisted in 20 kg of silage, 4 kg of lucerne and 16 kg of concentrate per cow and day. Lactating cows produced about 50 kg manure per day. Manure samples were taken from the lactating cow house, directly from the floor during the clean up operation (RMCH) and from the manure pit (RMP). The RMCH samples were kept in a lab pit during 30 days at ambient temperature. Vessels of 25 litres were employed as controlled dung pits and were provided with hydraulic closing systems in order to avoid the entrance of air, to prevent volatile fatty acids (VFA) oxidation and to allow the release of generated gas to prevent an excessive increase in pressure. The RMP samples were kept in similar lab pits at ambient temperature and were subjected to the separation process within a maximum of five days after its collection. In some tests, RMP samples were subjected to screening through a 1.5 mm mesh sieve. This operation aimed to remove

the larger solids, hardly biodegradable or non-biodegradable at all by natural processes. To facilitate the screening operation, tap water was added to the original sample in a proportion of one litre of water to four litres of manure sample. Diluted screened manure (DSM) is that resulting from having been screened, after the dilution procedure outlined above, by a static laboratory screen. The mean value of the TS content after screening was 60 kg m^{-3}, similar to the mean TS content obtained in farms that evacuate the wastes by flushing them with water and then subjecting the slurry to mechanical screening through a 1.5 mm mesh sieve. The mean values of manure samples are shown in Table 1. RMCH, RMP, DSM samples, as well as the solid and liquid fractions separated by flocculation and screening were kept at 4ºC until analytical tests were done.

Working with very heterogeneous samples typically leads to frequent discrepancies between the results obtained in experiments and those presented in reports related to the matter [22]. The mean concentrations for the RMCH samples were higher than the RMP, because of rain water dilution. The VS/TS ratio was higher in RMCH than RMP because degradation of easily biodegradable organic matter had started. In DSM samples, the VS/TS ratio was the lowest of all.

2.2. Analytical methods

Volatile fatty acids (VFA) were determined using an HP6890 GC apparatus fitted with a 2m x 3.175 mm glass column, liquid phase 10% AT 1000, packed with the solid support Chromosorb W-AW 80/100 mesh. Nitrogen was the carrier gas and a FID detector was installed. Gas composition was analyzed on a 2m Poropak T column in a HP 6890 GC System with helium as carrier gas and TCD detector. All other analyses were performed following the Standard Methods for the Analysis of Waters and Wastewaters [23]. All analyses were done in triplicate and the data shown in this study are mean values of the three values obtained. A maximum deviation of 3% was allowed between the three results and the mean. Whenever the differences between the three values obtained were higher than 3% of the mean, the analysis was repeated. Biodegradability of the liquid fraction was determined according to the method described by Field et al. [24] for wastewaters. Volatile fatty acids (acetic, propionic, butyric, isobutyric, valeric and isovaleric) concentration was converted to COD (COD_{VFA}) by using conversion factors for theoretical oxygen demand: 1.066 for acetic acid; 1.514 for propionic acid, 1.818 for butyric and isobutyric acid, and 2.039 for valeric and isovaleric acids. Analogously, the methane produced was converted to COD (COD_{CH4}) by the equivalence 1 kg COD = 0.350 m^3 CH_4. The calculated percentages of COD_{VFA} and CH_4 are the result of dividing their respective COD values by the initial value of the total COD (COD_0).

$$\%COD_{VFA} = \frac{COD_{VFA}}{COD_0} \cdot 100$$

$$\%COD_{CH4} = \frac{COD_{CH4}}{COD_0} \cdot 100$$

In this method, it is assumed that:

$$Non-VFA\ \ biodegradable\ \ Organic\ \ Matter \ \rightarrow\ \ VFA + acidogenic\ biomass$$

$$VFA \ \rightarrow\ \ CH_4 + methanogenic\ biomass$$

$$\%COD_{acid} = \%COD_{CH4} + \%COD_{VFA}$$

$$\%COD_{BD} = \%COD_{acid} + \%COD_{cell}$$

where COD_{acid} is the addition of COD due to VFA present and CH_4 produced. Biodegradable COD (COD_{BD}) is the sum of COD_{acid} and the COD_{cel}. This COD_{cel} takes into account the COD employed in the growth of both the acidogenic and methanogenic biomass.

$$\%COD_{cell} = (\%COD_{cell})_{acid} + (\%COD_{cell})_{meth}$$

$$(\%COD_{cell})_{acid} = \frac{Y_A}{1-Y_A} \cdot (\%COD_{acid} - \%COD_{VFA})$$

$$Y_A = 0.196\ \frac{g\ COD_{cell}}{g\ COD_{used}}$$

$$(\%COD_{cell})_{meth} = \frac{Y_M}{1-Y_M} \cdot \%COD_{CH4}$$

$$Y_M = 0.028\ \frac{g\ COD_{cell}}{g\ COD_{used}}$$

where Y_A and Y_M are the estimated cellular yield coefficients for acidogenic and methanogenic bacteria, respectively. The value of biodegradability after a 7-day test was considered to determine % COD_{BD}.

2.3. Experimental equipment

A lab-scale static screen with a sieve of 1.5 mm before flocculation, and 0.2 mm after flocculation, was used to separate solid and liquid fractions. To measure the anaerobic biodegradability of the LF, two cylindrical reactors, made of PVC, with an internal diameter of 22 cm, (2.5 litres total volume and 2.0 litres useful volume) were used. Stirring, at 0.33 Hz, was carried out for 20 seconds every 15 minutes by means of blade stirrers controlled by timing devices. For the methane productivity test, six reactors like those previously described were used, in this case without stirring. Two 1.0 litre bottles made of high density propylene, the tops of which were perforated in order to permit the release and recovery of biogas, were

used as a blank in the methane productivity test. Methane production was measured by means of a displacement system using an alkaline solution in order to absorb the CO_2 produced. Methane volumes are expressed at 293ºK and pressure of 101.15 kPa.

2.4. Preparation of flocculant solutions

The polyacrylamide used has the commercial name of Praestol K144L, a registered trademark of Ashland Chemicals. It is a copolymer of acrylamide (very strongly cationic). Commercial polyacrylamide (CP) was supplied in solid form by the company Stockhausen Iberia, S.A. Other flocculants supplied by the same company were used in previous studies, but the results obtained were worse. Although the manufacturer's recommendation was a 5 kg m^{-3} solution of polymer in tap water, the polymer was added to the samples as a 3 kg m^{-3} solution since it was observed that this concentration permitted an easier separation of SF and LF. The dose of polymer employed will be expressed as g CP kg^{-1} TS, where CP is the solid polymer added in form of solution (3 kg m^{-3}) and TS refers to the manure sample TS content.

2.5. Separation of solid and liquid fraction

The prepared polyacrylamide solution was mixed with the dairy cattle manure using two 1000 ml beakers (pouring method). This method was used due to the high solids concentration and the viscosity of the manure. The mixture, composed of the polymer solution and the sample, was passed successively from one beaker to the other a predetermined number of times, which depended on the solids concentration in the sample. When optimal flocculation was achieved, mixing was stopped and the sample was allowed to settle for 5 minutes. Then, liquid and solid fractions were separated using 0.2 mm mesh sieve, collecting the flocculated solid fraction and the liquid fraction separately. Generally, the best results were obtained when the volume of polymer solution was added gradually rather than all at once. Depending on the solids content, air can get clogged amongst the flocs, lifting them to the top. This can be avoided by a quick stirring to promote elimination of the clogged air.

3. Results and discussion

3.1. Evaluation of the optimal dose of CPE in solid-liquid separation tests

A set of preliminary tests was run to roughly determine the optimal dose of CP. From these results, the necessary dose was estimated according to the TS concentration of the samples. Later experiments were carried out, using a slightly lower or higher dose than that calculated previously, with the aim of accurately determining the optimum dose with the least possible number of tests. Mean values for TS and VS in the samples analysed during these experiments are shown in Table 1. The volume of each sample was 200 cm^3. In this case the concentration of the CP solution was 5 kg m^{-3}.

Table 2 shows the experimental values obtained in the separation of LF and SF for the RMP samples. The polymer dose is expressed as milligrams of solid polymer per gram of TS in manure samples (mg CP g^{-1} TS). The results obtained in the separation of LF and SF as TS removal percentages for the three kinds of samples analysed in this work were adjusted according to a Logistic Function. For TS, the equation of the model is given as a function where "x" is the flocculant dose, as g CP kg^{-1} TS.

$$TS_{removed} = \frac{a}{1 + b\exp^{-cx}}$$

Values obtained for constants are shown in Table 3. Figure 1 shows the removal percentages of TS Vs CP dose for RMCH. The optimum doses were 42.8, 43.9 and 43.6 g kg^{-1} for DSM, RMP and RMCH samples, respectively. The values for the optimum dose were very similar for RMP and RMCH samples, which had a similar TS content. For the DSM sample, the optimum dose was a little lower; this sample type was also the one with the lowest TS level. The TS removal efficiencies for the samples whose CP doses equal or surpass the optimum were 84.0% ± 0.2; 89.3% ± 0.5 and 93.3% ± 0.1 for DSM, RMP and RMCH, respectively.

In Figure 1, when the polymer dose is lower than the optimum, the TS removal percentage increases fast with growing doses; when dose value is close to the optimum, the removal percentage slows down and when the optimum dose is reached, it keeps constant. Comparing the results obtained with the different types of manure, a linear correlation (Figure 2) is observed between solids concentration in the sample to be treated and the removal percentage of TS using flocculant doses equal to or higher than 45 g kg^{-1}.

3.2. Trial of separation process

A dairy manure sample, taken from the cow house of the farm, was kept in a lab-scale manure pit for 30 days at laboratory temperature (293-296ºK). Previous experiments showed that after 30 days of storage at

ambient temperature, VFA concentration had increased; however, no methanization had occurred [20]. Thus, only the development of the hydrolytic and acidogenic stages were allowed. For this experiment, 10 kg of the stored dairy manure sample were subjected to a flocculation process with the reactive Praestol K144L, using a concentration of 3 kg m^{-3}. The minimum volume of polymer solution for which the separation of manure in solid and liquid fractions took place was determined. This dose was 19.8 g kg^{-1} of TS in manure. A lab-scale stationary screen like that described in Material and Methods (above) was used for dewatering the SF. The results of the separation process for 1.0 kg of raw dairy manure from the lab-scale manure pit can be seen in Table 4.

The mass of the SF separated was 29.1% of the mass of the original dairy manure and the polymer solution. The SF contained the majority of the TS (76.1%), VS (79.9%), TKN (59.4%) and TP (87.4%) of the initial content of the dairy manure. The rest of the initial components of the manure remained in the liquid fraction. The VS/TS ratio was 0.78 for dairy manure, 0.82 and 0.63 for SF and LF. The SF had a higher percentage of organic matter content than the dairy manure.

The percentage of TS, TKN and TP removed are in the same range as those reported, after coagulation-flocculation and screening operations, for 1.5% TS flushed dairy manure [10]. Removal percentages are higher than those obtained, without previous flocculation, by centrifugation [25].

Table 5 shows the characteristics of the liquid fraction. TS concentration was reduced from 101.2 kg m^{-3} for the dairy manure to 19.46 kg m^{-3} for the liquid fraction. After the flocculation process, the COD total (COD_T) concentration was 21.53 kg m^{-3}, and 18.50 kg m^{-3} was the value of $COD_{filtrate}$, due to organic matter in the soluble fraction obtained after filtering the LF. The percentage of COD_T due to $COD_{filtrate}$ was 85.9% after the flocculation treatment. Elimination of VFA is not desirable through the coagulation-flocculation process since they are biodegradable compounds transformable to methane. Regarding COD_{VFA}, in the LF this value was 75.5% of the COD_T. This high percentage of COD_T due to VFA leads us to expect a high percentage of COD removal and its conversion to methane in a posterior anaerobic treatment. There were three main VFA which contribute to COD_{VFA}: acetic acid, 45.3%; propionic acid, 22.6% and butyric acid, 17.8%. These percentages are in accordance with those found in the bibliography [26].

On the other hand, as data in Tables 4 and 5 shows, TKN and TP concentrations in the liquid fraction decreased from 4.18 and 0.81 kg m^{-3} in dairy manure to 1.48 and 0.07 kg m^{-3} in the liquid fraction respectively. This decrease in nutrient concentration in the LF is advantageous for anaerobic digestion since the removal of nitrogen and phosphorous nutrients is minimal during anaerobic process, which is

only due to cellular synthesis, struvite ($MgNH_4PO_4$) precipitation and NH_3 stripping, owing to a pH increase.

The TS content of the SF, shown in Table 4 is lower than the optimum (40-50%) for the development of the composting process [27]. Thus, it would be necessary to mix the SF with other wastes that contain higher solids content, such as straw and sawdust, to make treatment by the conventional aerobic composting process possible. Another option for this solid fraction is the semi-liquid anaerobic process in either batch or continuously fed systems.

For an industrial application with a decanter centrifuge, conducting a pre-screening process before flocculation would considerably diminish the polymer consumption to remove solids from the RMCH for two main reasons: on one hand the removal of solids in the process of screening, about 50% according to Rico et al. [7], and on the other hand the screened liquid fraction obtained would have a lower TS content, which means lower dose of polymer required. Carrying out the flocculation process with previous screening would allow a solid-liquid separation process with lower reactive consumption, and a resulting decrease in costs. In this work, the farm where manure was taken was equipped with an industrial manure separator that only could process the manure from the pit. Fresh manure daily removed from the cow house during cleaning operation could not be directly pumped to the separator. For anaerobic biodegradability and methanogenic productivity tests it is recommendable to use fresh manure. However laboratory scale is a very laborious task of screening, and the solid fraction obtained presents high moisture content.

Depending on the origin of the manure, time and conditions of storage, some differences in the composition and distribution may appear after solid-liquid separation. The longer the time and higher the temperature, the greater the amount of organic matter that would be in soluble form, organic nitrogen that would be converted into ammonia and biodegradable organic matter that would be transformed into VFA. If methanization takes place, VFA in the liquid fraction will decrease as the result of CH_4 formation.

3.3. Methane production

A set of batch assays were performed to determine the methane productivity of the manure, the solid fraction and the liquid fraction. Six reactors of 2.5 L, as described above, were employed and the experiments, carried out at 35ºC, were run in duplicate. 300 g of stabilised manure were put, as inoculums, with 1000 g of manure, SF or LF into each reactor. Two 1.0 L bottles, as described above, loaded with 300 g of the same stabilized manure and 0.5 L of tap water were used as blanks. The eight

363 reactors were placed in two thermostatic baths, four into each one, in order to achieve a temperature of
364 35ºC in the reactors. In all the cases, air was removed from the reactors by passing biogas through them.
365 During 90 days, the biogas produced in each reactor was collected in a gas meter as described above. The
366 results reported are the mean values from the two reactors with the same kind of sample, subtracting the
367 mean value of biogas blank production.

368 On day 90 the mean methane volumes accumulated were 25.21, 33.47 and 7.08 L kg^{-1} for dairy
369 manure, solid and liquid fractions, respectively. The results from both assays were coherent, reaching a
370 maximum difference of 2% for the solid fraction. In Figure 3, the evolution of the specific methane
371 production for each sample can be seen. These values were calculated from the accumulated methane
372 volumes and the VS values in Table 4. The final values were: 0.320, 0.258 and 0.580 m^3 kg^{-1} of VS for
373 dairy manure, solid and liquid fractions, respectively. The liquid fraction was the sample with the highest
374 specific methane production due to its high biodegradability. The manure reached an intermediate value,
375 while the solid fraction presented the lowest one, since the majority of the hardly biodegradable
376 compounds ended up in this fraction.

377 The methanogenic productivity found in this assay for dairy manure (0.320 m^3 kg^{-1} of VS) is higher
378 than others found in the bibliography [24]. It must be taken into account that when VS content is
379 measured in dairy manure, there is a high fraction of volatile organic components such as VFA. The VS
380 measurement includes drying (105ºC) and incineration (550ºC). During drying operations, VFA losses
381 can be expected for dairy manure depending on sample pH values. This means that only 25% of the VFA
382 present could have been included in the VS measurement [28]. In addition, methane production was
383 minimised in the controlled manure pit. For these reasons, the specific levels of methane production for
384 these samples of dairy manure, solid and liquid fraction were higher. The specific methane production
385 increased for the liquid fraction because the easily biodegradable components were not removed by the
386 physical-chemical treatment.

387 Figure 4 represents the methane production from 1 kg of manure, 25.21 dm^3. It is worth taking into
388 account that 1 kg of manure, after the floccu1ation treatment, resulted in 0.485 kg of SF and 1.168 kg of
389 LF. The solid and liquid fractions derived from 1 kg of manure yielded 16.24 and 8.27 L of methane
390 respectively, which results in 24.51 L, a 2.8% less than non separated manure. This small difference can
391 be attributed to experimental errors. That represented 64.4% and 32.8% for solid and liquid fractions
392 respectively, with regards to methane production from 1 kg of manure. So, approximately two thirds of
393 methane yield were produced by the solid fraction whereas liquid fraction produced the third part of the
394 methane yielded by non-separated manure.

Separation of liquid and solid fractions by means of coagulation-flocculation decreased the total production of methane per mass unit for the separated liquid fraction. However the specific methane production considerably increased. On the other hand, for the solid fraction the methane production per mass unit increased but the specific methane production decreased. The important issue is the fact that now the time required to convert the biodegradable organic matter into methane for the liquid fraction diminished as the majority of the hardly biodegradable organic matter was removed. The liquid fraction had yielded 90% of the final methane production after 21 days, whereas the manure and the solid fraction required 48 and 52 days to reach this percentage, respectively.

The methane yield also depends on the origin of the manure, time and conditions of storage, pre-treatments and the amount of seeding employed in methanogenic production assays. Raising active seeded biomass increases organic matter employed in biochemical methanogenic reactions and diminishes the organic matter used in cell synthesis processes.

3.4. Biodegradability of liquid fraction

The same liquid fraction obtained by the treatment of 10 kg of dairy manure from the lab-scale manure pit was subjected to an anaerobic biodegradability test at 35ºC. In this way, the percentage of anaerobic biodegradable COD for the liquid fraction was determined.

Two reactors were used to test the anaerobic biodegradability of the liquid fraction. One reactor operated as a blank (300 g of biomass and 1 litre of tap water). The other was the treatment reactor (300 g of biomass and of 1 litre of liquid fraction). Biomass from a UASB lab-scale reactor, treating leachates from a composting plant (operating at 35ºC), was used as seed biomass. The main characteristics of these leachates were the high concentrations of VFA and NH_4^+-N. A VS concentration of 62.5 g kg^{-1} and a specific methanogenic activity in terms of COD_{CH4} at 35ºC of 590 g kg^{-1} d^{-1} of VS were observed for this biomass. Air was removed from reactors by passing biogas through them. To measure the biogas produced, two gas meters of the type described in material and methods section were used. On days 4 and 7, samples were withdrawn to measure COD_T, $COD_{filtrate}$ and the COD_{VFA}, calculating, as well, the COD equivalent to the methane produced (COD_{CH4}). Corrected values were obtained from the data of the treatment reactor minus the data of the blank reactor. On day 8, one litre of supernatant was withdrawn from the treatment reactor and another litre of liquid fraction was added to the reactor. The biodegradability test was carried out again.

To determine the percentage of COD_{BD}, the corrected values obtained on day 7 were considered. The percentage of COD_{CH4} values were 83.0 and 83.5% in the first and second assay, respectively. The mean value for the percentage of COD_{CH4} was 83.3%. For the liquid fraction, the percentages of anaerobic COD_{BD} were 87.2 and 87.8%, respectively.

Table 6 shows corrected data from the reactor corresponding to the test that resulted in a percentage of COD_{BD} of 87.2. Taking into account the high methanogenic activity of the biomass used as seed (11.2 g COD_{CH4} d^{-1}), the calculated theoretical percentage of COD_{cel} could not be considered, giving a more conservative value, 83.0 for % COD_{BD}. Taking into account the relation between the mass of the treated liquid fraction and biomass in the anaerobic biodegradability test, it is very probable that this liquid fraction could be satisfactorily treated in high load reactors, like UASB, operating with HRT shorter than two days.

Volumes of methane produced in both kinds of liquid fraction tests, methane production and anaerobic biodegradability, were coherent. In biodegradability tests, a mean value of 6.94 L CH_4 kg^{-1} LF was produced, whereas, in the methanogenic production assays, the mean value was 7.08 L CH_4 kg^{-1} LF. The methane production in the methanogenic production test was a bit higher than that obtained in the anaerobic biodegradability test, perhaps due to the different amount and origin of biomass used or the different duration of the two kinds of tests.

4. Conclusions

Flocculation of dairy cattle manure with TS concentrations up to 140 g kg^{-1} by additions of a strong cationic polyacrylamide flocculant allows the elimination of up to 90% of total solids, using optimum doses of approximately 43.9 g kg^{-1} of TS. Elimination percentages increase in a linear way with solid concentrations. The solid fraction retained 29.1% of total initial mass, as well as 76.1% of TS and 79.9% of VS. In addition, 59.4 and 87.4% of TKN and TP respectively, were retained in the solid fraction.

Methane production from the untreated manure was 0.320 m^3 kg^{-1} of VS. Liquid and solid fractions yielded 0.580 and 0.258 m^3 kg^{-1} of VS, respectively. Due to its higher VS contents, the solid fraction yielded twice the amount of methane than the liquid fraction. The anaerobic biodegradability of the liquid fractions obtained was 83.0%, considerably higher than the value corresponding to manure (around 50%). Taking into account these properties, the LF could be subjected to anaerobic process in high load reactors.

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6. References

[1] Burton CH. Manure management: Treatment Strategies for Sustainable Agriculture. Wrest Park, Silsoe, Bedford, UK: Silsoe Research Institute; 1997. 196 pp.

[2] Poulsen HD, Børsting CF, Rom HB, Sommer SG. Nitrogen, phosphorus and potassium content of manure. Viborg, Denmark: Danish Institute of Agriculture Science; 2001. 152 pp. DIAS Report No.: 36.

[3] Williamson JC, Taylor MD, Torrens RS, Vojvodic-Vukovic M. Reducing nitrogen leaching from dairy farm effluent-irrigated pasture using dicyandiamide: a lysimeter study. Agric Ecosyst Environ 1998;69(1):81-8.

[4] Møller HB, Lund I, Sommer SG. Solid-liquid separation of livestock slurry: efficiency and cost. Bioresour Technol 2000;74(3):223-9.

[5] Henriksen K, Berthelsen L, Matzen R. Separation of liquid pig manure by flocculation and ion exchange. Part 1: laboratory experiments. J Agric Eng Res 1998; 69(2):115-25.

[6] Lo KV, Lau A, Liao PH. Composting of separated solid swine wastes. J Agric Eng Res 1993;54(4):307-17.

[7] Rico C, Rico JL, Tejero I, Muñoz N, Gómez B. Anaerobic digestion of the liquid fraction of dairy manure in pilot plant for biogas production: Residual methane yield of digestate. Waste Manage 2011;31(9-10):2167–73.

[8] Zhang RH, Westerman PW. Solid-liquid separation of animal manure for odor control and nutrient management. Appl Eng Agric 1997;13(5):657-64.

[9] Chang AC, Rible JM. Particle size distribution of livestock wastes. Proceedings of the Third Inter Symposium on Livestock Wastes: ASAE; 1975. 4 pp.

[10] Power WJ, Montoya RE, Van Horn HH, Nordstedt RA, Bucklin RA. Separation of manure solids from simulated flushed manures by screening or sedimentation. Appl Eng in Agric 1995;11(3):431-6.

[11] Zhang RH, Lei F. Chemical treatment of animal manure for solid-liquid separation. T ASAE 1998;41(4):1103-8.

[12] Holmberg RD, Hill DT, Prince TJ, Van Dyke NJ. Potential of solid-liquid separation of swine wastes for methane production. T ASAE 1983;26(6):1803-7.

[13] Pain BF, Hepherd RQ, Pittman RJ. Factors affecting the performance of four slurry separating machines. J Agric Eng Res 1978;23(3):231-42.

[14] Hjorth M, Christensen KV, Christensen ML, Sommer SG. Solid–liquid separation of animal slurry in theory and practice. A review. Agron Sustain Dev 2010;30(1):153-80.

[15] Hjorth M, Christensen ML, Christensen PV. Flocculation, coagulation, and precipitation of manure affecting three separation techniques. Bioresour Technol 2008;99(18):8598-604.

[16] Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P. The future of anaerobic digestion and biogas utilization. Bioresour Technol 2009;100(22):5478–84.

[17] Frear C, Wang ZW, Li C, Chena S. Biogas potential and microbial population distributions in flushed dairy manure and implications on anaerobic digestion technology. J Chem Technol Biotechnol 2011;86(1):145-52.

[18] Dugba PN, Zhang R. Treatment of dairy wastewater with two-stage anaerobic sequencing batch reactor systems-thermophilic versus mesophilic operations. Bioresour Technol 1999;68(3):225–33.

[19] Kalyuzhnyi S, Sklyar V, Fedorovich V, Kovalev A, Nozhevnikova A, Klapwijk A. The development biological methods for utilisation and treatment of diluted manure streams. Wat Sci Technol 1999;40(1):223-9.

[20] Rico C, García H, Rico JL, Fernández J, Renedo J. Evolution of composition of dairy manure supernatant in a controlled dung pit. Environ Technol 2009;30(13):1351–9.

[21] Weiland P. Biomass digestion in agriculture: a successful pathway for the energy production and waste treatment in Germany. Eng Life Sci 2006;6(3):302–9.

[22] Dou Z, Galligan DT, Allshoyuse RD, Toth JD, Ramberg CFJ, Ferguson JD. Manure sampling for nutrient analysis: variability and sampling efficacy. J Envin Qual 2001;30(4):1432-7.

[23] Standard methods for the Examination of Water and Wastewater. 19th edn, American Public Health Association/American Water Works Association/ Water Environment federation, Washington DC, USA; 1995.

[24] Field J, Sierra R, Lettinga G. Ensayos anaerobios. 4º Seminario de Depuración Anaerobia de Aguas Residuales. Universidad Valladolid: Secretariado de Publicaciones; 1988. 30 pp.

518 [25] Møller HB, Sommer SG, Ahring BK. Separation efficiency and particle size distribution in relation
519 to manure type and storage conditions. Bioresour Technol 2002;85(2):189-96.
520 [26] Patni NK, Jui PY. Volatile fatty acids in stored dairy-cattle slurry. Agric Wastes 1985;13(3):159-78.
521 [27] Brito LM, Coutinho J, Smith SR. Methods to improve the composting process of the solid fraction of
522 dairy cattle slurry. Bioresour Technol 2008;99(18):8955-60.
523 [28] Derikx PJL, Willer HC, Ten Have PJW. Effect of pH on the behaviour of volatile compounds in
524 organic manures during dry-matter determination. Bioresour Technol 1994;49(1):41-5.
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